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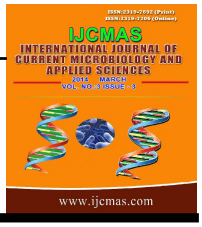

Original Research Article

Anti-Corrosive effect of N-[(benzylidene hydrazino)-propyl]- benzotriazole and N-[(4-oxo-2-phenyl-1,3-thiazolidineimino)-propyl]-benzotriazole for admiralty brass in marine environment

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Keywords

Admiralty brass, artificial sea water, SEM, BTA derivatives, polarisation.

A B S T R A C T

Benzotriazole derivatives, namely N-[(benzylidene hydrazino)-propyl]-benzotriazole(BPBT) and N-[(4-oxo-2-phenyl-1,3-thiazolidineimino)-propyl]-benzotriazole (OPBT) were synthesised and their inhibition behaviour on admiralty brass in artificial sea water were investigated by the weight-loss method and potentiodynamic polarisation methods. Benzotriazole derivatives were found to act as mixed type inhibitors. Of the compounds studied, OPBT exhibited the best performance, giving more than 94% inhibition efficiency in artificial sea water. Solution analysis revealed the dissolution of both copper and zinc occurred in the presence of the inhibitors. The morphology of the brass after corrosion in the presence and absence of the BTA derivatives was examined using scanning electron microscopy (SEM). The percentage composition of the brass surface was analyzed using energy dispersive X-ray analysis (EDAX).

Introduction

Copper and its alloys are used extensively and successfully in many types of chemical equipment including evaporators, pumps, valves, fans and fractionating columns. Large quantities of pipes made out of copper and copper alloys are used to make condensers and heat exchangers, where fresh or salt water is used for cooling (Quartarone et al., 1998). Brass is susceptible to a corrosion process known as dezincification and this tendency increases with increasing zinc content of the brass, (Shukla and Pitre, 2002). During the past decade, many techniques have been used to minimise the dezincification and corrosion of brass. One of the techniques for minimising corrosion is the use of inhibitors. The effectiveness of the inhibitor varies with its concentration, the corrosive medium and the surface properties of the alloy. Many inhibitors have been used to minimise the corrosion of brass in different media (Elmorsi et al., 1999).

Benzotriazole, for example, has been studied and found to have excellent inhibition properties in several corrosive environments, (Al-kharafi et al., 2002). This molecule contains nitrogen atoms and has been found useful in preventing copper staining and tarnishing. The effectiveness of BTA has been related to the formation of a $[Cu^{+} BTA^{-}]_n$ film. The film is considered to be insoluble and polymeric, (Tromans et al., 1997). Bag et al., (1996), investigated the protective action of azole derivatives on the corrosion and dezincification of 70/30 brass in ammonia solution and concluded that the inhibitors could control corrosion.

The aim of present investigation was to study the inhibition efficiencies of N-[(benzylidene hydrazino)-propyl]-benzotriazole(BPPT) and N-[(4-oxo-2-phenyl-1,3-thiazolidineimino)-propyl]-benzotriazole (OPBT) on the corrosion and dezincification of admiralty brass in artificial sea water. Interest in chloride media relates to the applicability of brass as the tubing material for condensers and heat exchangers in cooling water systems. For the corrosion study, weight-loss, electrochemical tests, such as potentiodynamic polarisation and solution analysis were used. The morphology of the brass surface examined by scanning electron microscopy (SEM) also was considered. The percentage composition of the brass surface was analyzed using energy dispersive X-ray analysis (EDX).

Materials and Methods

Materials

The material used for this study was admiralty brass supplied in the form of sheet and the chemical composition (weight percent) of the admiralty brass was 70.34% Cu, 28.53% Zn, 0.92% Sn, 0.069% Pb, 0.058% Fe and traces of Mn, Ni & As, as analyzed by optical emission spectrophotometry. The artificial seawater was prepared by dissolving the chemicals (23.9849g NaCl, 5.0290 g $MgCl_2$, 4.0111 g Na_2SO_4, 1.1409 g $CaCl_2$, 0.6986g KCl, 0.1722g $NaHCO_3$, 0.100 g KBr,0.0143 g $SrCl_2$ and 0.0254 g H_3BO_3) in 1 litre of distilled water [Milero, 1996]. The inhibitors N-[(benzylidene hydrazino)-propyl]-benzotriazole and N-[(4-oxo-2-phenyl-1,3-thiazolidineimino)-propyl]-benzotriazole were synthesized according to the reported procedures (Adesh Dubey et et al.,2011) and their structures are shown in the scheme 1.

Synthesis of N-[(benzylidene hydrazino)-propyl]- benzotriazole (BPBT)

A mixture of N-(hydrazino propyl)-benzotriazole (2g, 0.01 mol) and benzaldehyde (1.11g, 0.01 mol) in methanol (20 mL) in the presence of a catalytic amount of glacial acetic acid was refluxed for 5.3 hrs. The solvent was removed under reduced pressure to and the resulting crude product was purified by passing it through a chromatographic column packed with silica gel using chloroform: methanol (8:2 v/v) as eluant. Resulting purified product was recrystallized by chloroform to give compound.

Synthesis of N-[(4-oxo-2-phenyl-1,3-thiazolidineimino)-propyl]-benzotriazole (OPBT)

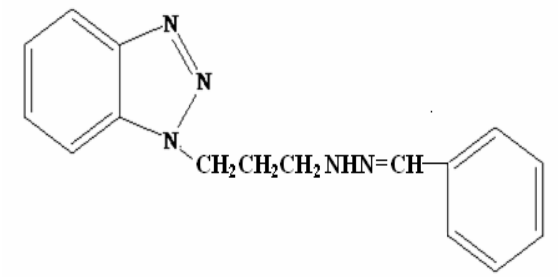
A mixture of compound N-[(benzylidene hydrazino)-propyl]- benzotriazole(BPBT) (1g, 0.003 mol) and SHCH2COOH(0.331g 0.003 mol) in methanol (20 mL) containing a pinch of anhy. ZnCl2 was first stirred for about 2 hours followed by

refluxing on a steam bath for about 6 hrs. The recation mixture was cooled and excess of solvent was evaporated under reduced pressure. The solid crude product was purified by passing it through a chromatographic column packed with silica gel using chloroform: methonal (8:2v/v) as eluant and again purified by recrystallisation from ethanol to give compound N-[(4-oxo-2-phenyl-1,3-thiazolidineimino)-propyl]-benzotriazole.

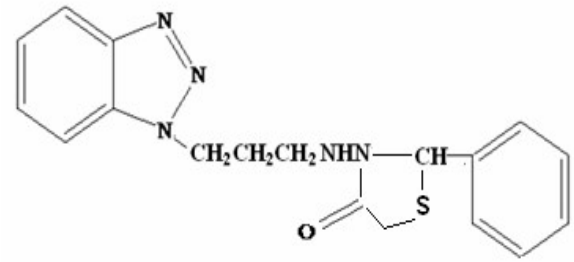
Methods

For the weight-loss method, the brass specimens (4 cm x 2.5 cm x 0.2 cm) were abraded with silicon carbide papers (120-1200grit), thoroughly washed with distilled water, degreased with acetone, rinsed with distilled water, dried and weighed. The specimens were immersed in 300 ml of artificial sea water, with and without inhibitors at 30^{o}C for 45days.

N-[(benzylidene hydrazino)-propyl]-benzotriazole (BPPT)



N-[(4-oxo-2-phenyl-1,3-thiazolidineimino)-propyl]-benzotriazole(OPBT)



For electrochemical studies, the working electrode with an area of 1cm^2 was embedded in epoxy resin in a Teflon holder. The electrode was abraded mechanically with silicon carbide papers from 120 to 1200 grit followed by polishing with 5 μm diamond paste. The electrode was thoroughly washed with double distilled water, degreased in acetone for 15 minutes using ultrasonic vibration, rinsed with distilled water and dried. The cell assembly consisted of brass as working electrode, a platinum foil as counter electrode and a saturated calomel electrode (SCE) as a reference electrode with a Luggin capillary bridge.

Polarization studies were carried out using a Vibrant potentiostat/ galvanostat model No. VSM/CS/30 at a scan rate of 1mV/s.. The working electrode was immersed in artificial sea water (open atmosphere) and allowed to stabilize for 30 minutes (Ravichandran and Rajendran, 2005). In each case a potential of -1500 mV was then applied for 15 minutes to reduce oxides. The cathodic and anodic polarization curves for brass specimen in the test solution with and without inhibitors were recorded between –500 to 500 mV at a scan rate of 1 mV/s. The inhibition efficiencies of the compounds were determined from corrosion current density using the Tafel extrapolation method.

During the anodic polarization, metal dissolution takes place releasing considerable amounts of metal ions from the material. Hence, the solutions were analyzed to determine the leaching characteristics of the brass alloys. The solution left after polarization measurement was analyzed for copper and zinc by inductively coupled argon plasma-atomic emission spectroscopy (ICP-AES).

Solutions containing the optimum concentration of the inhibitor were chosen and a blank was also analyzed for comparision purposes. The morphology and composition of the brass surface after polarization measurements was analyzed using JOEL^{R} JSM 35C SEM combined EDAX.

Results and Discussion

Weight-loss method

The corrosion rates and inhibition efficiencies of brass with different concentrations of BPBT and OPBT in artificial sea water at room temperature (30^{o}C) are given in Table 1. The corrosion rate (CR) and percentage inhibition efficiency (IE %) were calculated using the following equation (Fontana, 1987).

$$IE\% = \frac{CR_{(bl)} - CR_{(inh)}}{CR_{(bl)}} \times 100$$

where W is the weight-loss, D is the density, T is the immersion time, A is the area of the specimen and $CR_{(inh)}$ and $CR_{(bl)}$ are the corrosion rate of brass in the presence and absence of inhibitors respectively. The inhibition efficiency increases with increase in concentration of the inhibitors. The maximum IE% of each compound was achieved at 300 ppm, and a further increase in concentration showed only a marginal change in the performance of the inhibitor. The optimum of concentration of the inhibitors was 300 ppm and OPBT was superior to BPBT.

Mechanism of corrosion inhibition

The dissolution and film formation of brass in artificial sea water takes place via the reactions outlined below.

In the initial corrosion stage, zinc forms ZnO as a result of

$$Zn + H_2O = ZnO + 2H^+ + 2e^-$$

and copper forms Cu_2O as a result of

$$2Cu + H_2O = Cu_2O + 2H^+ + 2e^-$$

Thus a passive oxide film consisting of both Cu_2O and ZnO covers the surface. However, CuCl is formed on the surface (in the presence of chloride) by the reaction

$$Cu^+ + Cl^- = CuCl$$

which may ultimately result in the formation of $CuCl_2$ complex via

$$CuCl + Cl^- = CuCl_2^-$$

The effectiveness of BTA derivatives as corrosion inhibitors for brass can be gauged from the electrochemical behaviour of brass in artificial sea water.

The nature of the interaction of inhibitor on the metal surface during corrosion inhibition has been deduced in terms of the adsorption characteristics. In most cases the adsorption of inhibitor from the corrosive medium is a quasi-substitution process.

$$Inhibitor\ (soln) + nH_2O\ (ads) = Inhibitor\ (ads) + H_2O\ (soln)$$

The BTA derivatives are chemisorbed on the metal surface and that this chemisorbed layer prevents adsorption of oxygen and oxide formation. The protective film is a 1:1 complex of Cu (I) and BTA. The film is probably polymeric, in which BTA bridges two copper atoms via N_1 and N_3 and the aromatic ring is aligned parallel to the metal surface. Formation Cu (II) complexes also can occur, but they do not be protective. Chadwick et al concluded that zinc is also

incorporated into the surface film in significant quantities.

BTA derivatives inhibits by a two-fold mechanism. The chemisorbed film has a hydrophobic backbone that limits the transport of hydrated aggressive ions to the metal surface. Once formed, the film stabilized Cu (I) ions by means of an electronic effect, network formation or both.

It is well known that the inhibitive action of organic compound containing S, N and/or O is due to the formation of a co-ordinate type of bond between the metal and the lone pair of electrons present in the additive. The tendency to form co-ordinate bond and hence the extent of inhibition can be enhanced by increasing the effective electron density at the functional group of the additive. In aromatic or heterocyclic ring compounds, the effective electron density at the functional group can be varied by introducing different substituents in the ring leading to variations of the molecular structure**.** Based on the results, both BPBT and OPBT showed better inhibition efficiencies, due to the presence of heteroatom such as N, O, S and π electrons on aromatic nuclei. When compared to BPBT, OPBT showed highest inhibition efficiency, which may be due to the presence of S atom and high molecular weight and possessed by the OPBT molecule. The higher inhibition efficiency of the organic compounds are due to the basis of donor-acceptor interactions between the π electrons of the inhibitor and the vacant d-orbital of copper surface or an interaction of inhibitor with already adsorbed chloride ions.

Polarization studies

The cathodic and anodic polarization curves of admiralty brass in artificial sea water containing different concentrations of BPBT and OPBT are shown in Figure 1 and 2. It is evident that in the presence of inhibitor, the cathodic and anodic curves were shifted towards noble direction and the shift was found to be dependent on inhibitor concentration. Tables 2 illustrate the corresponding electrochemical parameters. The E_{corr} values were marginally shifted in the presence of BPBT and OPBT, which clearly indicated that the inhibitors control both cathodic and anodic reactions and thus act as mixed type inhibitors. The current density also decreased with increasing concentrations of the inhibitors. The corrosion rates and inhibition efficiencies (Tamilselvi et al., 2003) were calculated from polarization curves using the following equation.

$$CR = \frac{3.27 \times 10^{-3} \times I_{corr} \times EW}{D}$$

$$IE\% = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100$$

Where CR is the corrosion rate (mmpy), D is the density (g cm^{-3}), EW is the equivalent weight of the specimen, IE is the inhibition efficiency and $I_{corr\ (inh)}$ and I_{corr} are corrosion current density in the presence and absence of inhibitors respectively.

The values of cathodic Tafel slope (b_c) and anodic Tafel slope (b_a) of benzotriazole derivatives are found to change with inhibitor concentration, which clearly indicates that the inhibitors controlled both the reactions. The inhibition efficiency of BPBT and OPBT in artificial sea water attained a maximum value at 300 ppm.

The values of inhibition efficiency increase with increasing concentration of inhibitor, indicating that a higher surface coverage was obtained in the solution with the optimum concentration of inhibitor. The corrosion rate of admiralty brass in artificial sea water was found to be 11.32 x 10^{-2} mmpy and it was minimized by adding the inhibitors to a lower value of 1.15 x 10^{-2} mmpy and 0.64 x 10^{-2} mmpy due to the adsorption of BPBT and OPBT on the metal surface respectively.

A comparison of the values of inhibition efficiency obtained by weight loss measurements and polarization studies bring out clearly the fact that there is a fairly good agreement between these values. It is also found that the compounds function more effectively on the corrosion inhibition of admiralty brass in artificial seawater.

Accelerated leaching studies (ICP-AES)

The results of solution analysis and the corresponding dezincification factor (z) in the presence and absence of benzotriazole derivatives at their optimum concentration level in natural sea water for brass are given in Table 3. The dezincification factor (z) was calculated using the relation.

$$z = \frac{(Zn/Cu)_{sol}}{(Zn/Cu)_{alloy}}$$

Where, the ratio $(Zn/Cu)_{sol}$ is determined from solution analysis and $(Zn/Cu)_{alloy}$ is the ratio of weight-percent in the alloy (Abbas, 1991).

Figure 3 represent the effect of inhibitors on the dissolution of brass in natural sea water. From the figure, it can be observed that both copper and zinc were present in the solution whereas in the presence of inhibitors, which are able to minimize the dissolution of both copper and zinc. The data recorded in tables illustrate that the percent inhibition efficiency against the dissolution of zinc was correspondingly high as compared to the dissolution of copper. This indicates the excellent inhibition efficiency of inhibitors to prevent the dezincification of brass in natural sea water, which is also reflected in the values of dezincification factor. Among the inhibitors studied, OPBT shows highest inhibition efficiency in the dissolution of brass in artificial sea water. The percent inhibition efficiency against the dissolution of Zn was correspondingly high i.e. 96.92% can be achieved in the presence of OPBT containing natural sea water for brass, indicating that the preferential dissolution of zinc was almost completely minimized.

Surface composition analysis

The surface composition (wt.%) of the alloy in the presence and absence of inhibitors after polarization are given in Table 4. In the absence of inhibitors, the % of Cu and Zn are present in the surface were reduced due to the leaching of metal ions in sea water. Moreover, the higher concentration of chloride ions on the surface shows the penetration of Cl^- ions from the electrolyte. However, in the presence of BPBT and OPBT, the % of Cu & Zn is closer to that of the bulk composition of the alloy. Based on the surface analysis, these inhibitors exhibited excellent inhibition efficiency in sea water.

Morphological examinations

Figures 4 show SEM photographs of the brass surface in the absence and presence

Table.1 Inhibition efficiency at different concentrations of BPBT and OPBT on admiralty brass in artificial sea water

Inhibitor concentration (ppm)	Corrosion rate x 10^{-2} (mmpy)	Inhibition efficiency (%)
Blank	11.26	-
BPBT		
100	4.96	55.95
200	2.87	74.51
300	1.09	90.32
400	1.10	90.23
OPBT		
100	4.12	63.41
200	2.02	82.06
300	0.63	94.40
400	0.65	94.23

Table.2 Tafel polarisation parameters for the corrosion of admiralty brass in artificial sea water containing different concentrations of BPBT and OPBT

Inhibitor Concentration / ppm	E_{corr} (mV vs. SCE)	b_a /mV $(dec)^{-1}$	$-b_c$ /mV $(dec)^{-1}$	I_{corr} /μA cm^{-2}	Corrosion Rate / mmpy x 10^{-2}	Inhibition Efficiency / %
Blank	-314	48	35	8.97	11.32	-
BPBT						
100	-256	57	48	3.72	4.69	58.53
200	-235	68	56	2.53	3.19	71.79
300	-217	77	62	0.91	1.15	89.85
400	-218	76	63	0.93	1.17	89.63
OPBT						
100	-250	69	54	3.31	4.18	63.10
200	-227	74	65	1.92	2.42	78.59
300	-206	92	88	0.51	0.64	94.31
400	-208	90	86	0.54	0.68	93.38

Fig.1 Polarization curves of admiralty brass in artificial sea water containing different concentrations of BPBT

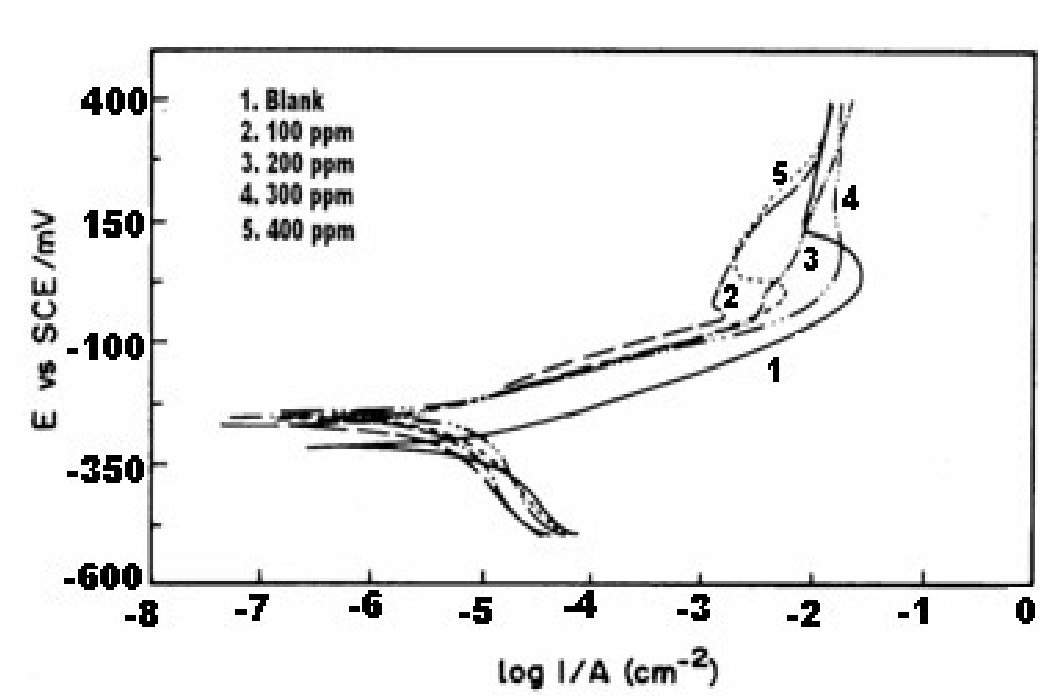


Fig.2 Polarization curves of admiralty brass in artificial sea water containing different concentrations of OPBT

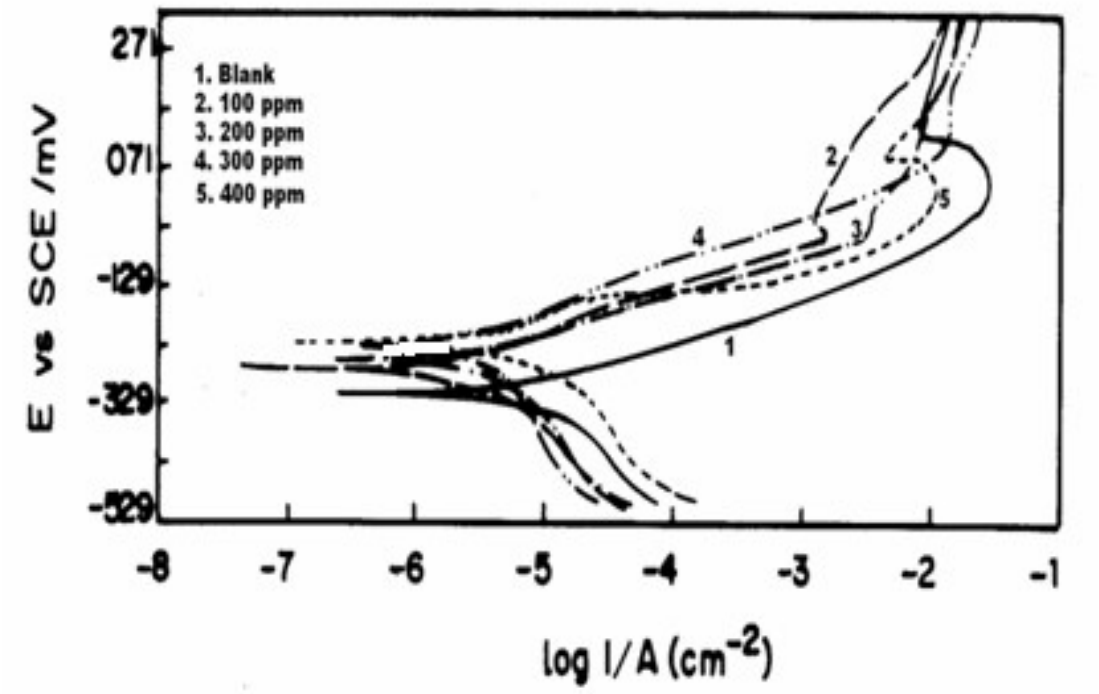


Fig.3 Concentration of copper and zinc leached out from brass in artificial sea water containing optimum concentration BPBT and OPBT.

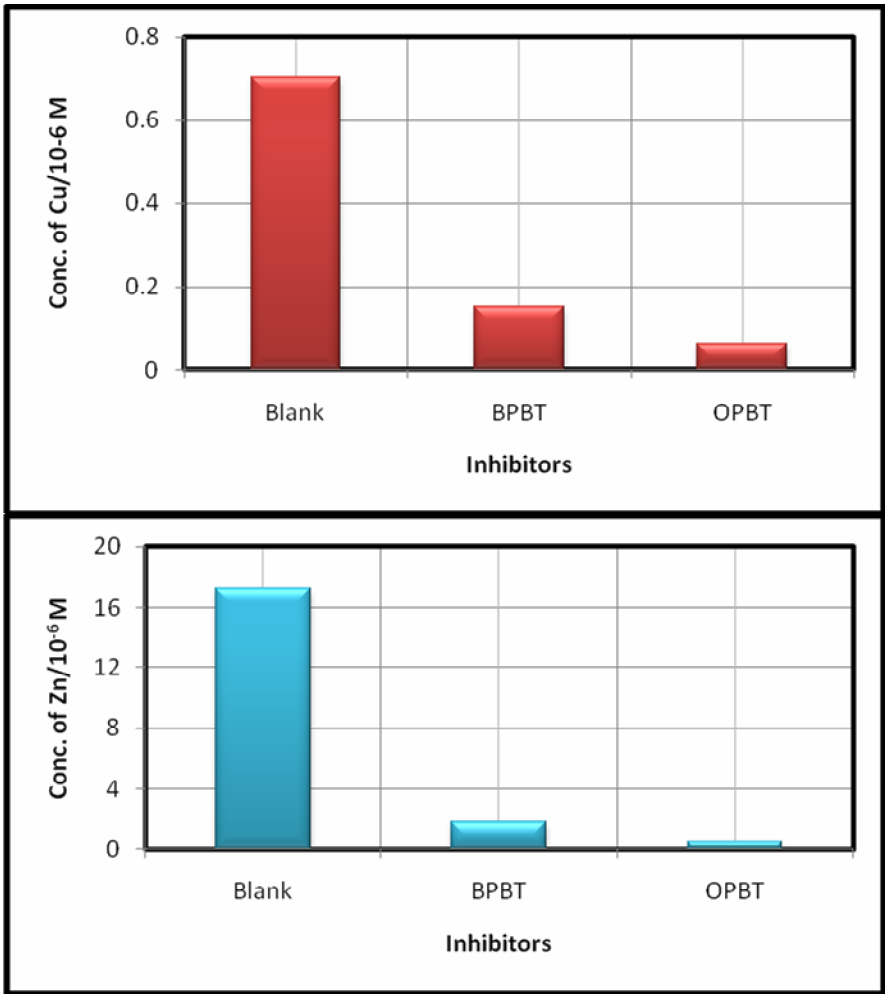


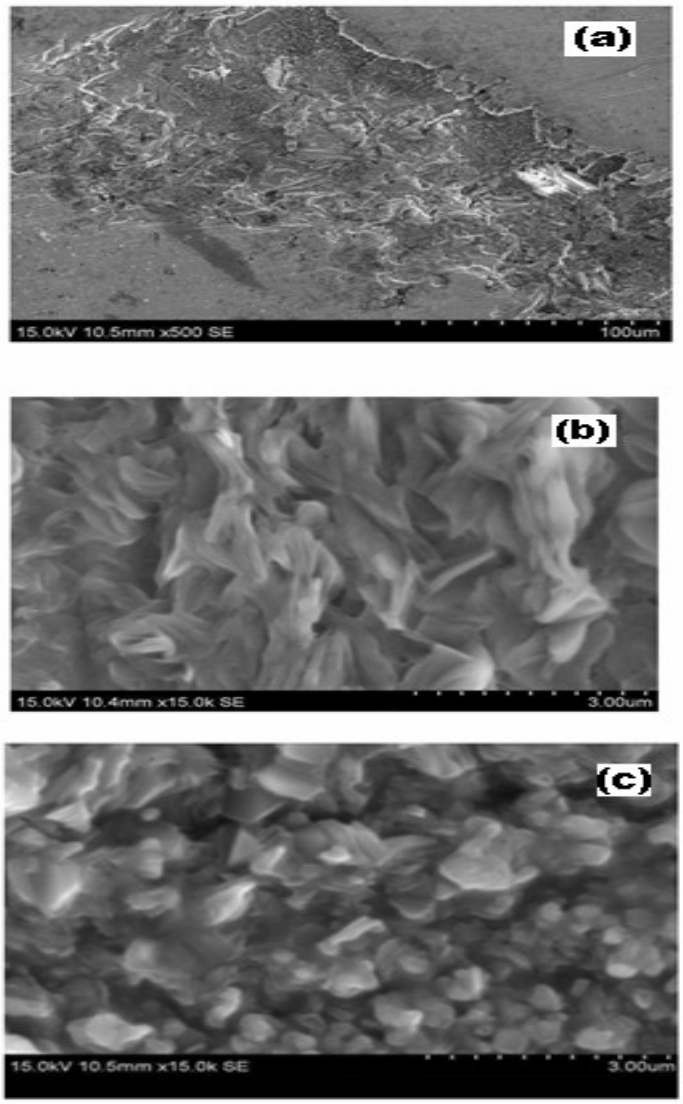
Table.3 Effect of optimum concentrations of BPBT and OPBT on the dezincification of admiralty brass in artificial sea water.

Inhibitors	Concentration		Dezincification factor (z)	Percent inhibition	
	Cu (10^{-6}M)	Zn (10^{-6}M)		Cu (%)	Zn (%)
Blank	0.703	17.21	60.36	-	-
BPBT	0.153	1.84	29.65	78.24	89.72
OPBT	0.063	0.53	20.74	91.03	96.92

Table.4 Surface composition (%) of admiralty brass in artificial seawater after polarization with optimum concentration of inhibitors

Inhibitors	Cu / %	Zn / %	Cl / %
Alloy	70.34	28.53	-
Blank	64.32	20.19	14.46
BPBT	68.83	27.04	2.98
OPBT	70.14	27.48	1.24

Fig.4 SEM images of admiralty brass in the absence (a) and in the presence of BPBT (b); OPBT(c)



of BPBT and OPBT after polarisation in artificial sea water. In the absence of inhibitors, extensive general corrosion occurred. The SEM micrograph of the

brass exposed to artificial sea water (Fig. (4a)) showed that the corrosion products covered the metal surface. Examination of the features shown in Figure 4(b) and 4(c) revealed that the specimen immersed in sea water containing additives, the inhibitor molecules adsorbed on the metal surface, thereby forming a compact surface film, which hinders the penetration of aggressive species into the metal surface, attributed to the better corrosion inhibition on the brass. In the presence of BTA derivatives, the corrosion decreased considerably.

Conclusions

The following conclusions were drawn from the present study:

The substituted benzotriazole derivatives (both BPBT and OPBT) showed good inhibition efficiency in artificial sea water.

The potentiodynamic polarisation studies showed that the inhibitors were mixed-type for brass in chloride solution. They decreased the anodic reaction rate more strongly than the cathodic reaction rate and rendered the open circuit potential more positive in artificial sea water.

The benzotriazole derivatives easily adsorbed onto the brass surface at the corrosion potential and formed a protective complex with the Cu(I) ion, thereby reducing the susceptibility of brass to corrosion.

Solution analysis reveals that the BPBT and OPBT were highly effective in preventing the dezincification of brass.

SEM studies confirm the presence of protective BTA film on the alloy surface.

EDAX analysis clearly proved that the inhibition is due to the formation of an insoluble stable film through the process of complexation of the substituted BTA molecules.

Acknowledgement

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